

PTO 09-0355

CC=JP
DATE=19800612
KIND=KOKAI
PN=55078073

HEAT-RESISTANT COATING
[TAINETSU TORYOU]

TOYONOBU MIZUTANI et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. OCTOBER 2008
TRANSLATED BY: SCHREIBER TRANSLATION, INC.

PUBLICATION COUNTRY	(10):	JP
DOCUMENT NUMBER	(11):	55078073
DOCUMENT KIND	(12):	KOKAI
PUBLICATION DATE	(43):	19800612
APPLICATION NUMBER	(21):	53-152871
APPLICATION DATE	(22):	19781209
INTERNATIONAL CLASSIFICATION	(51):	C 09 d 5/18 7/12
PRIORITY COUNTRY	(33):	
PRIORITY NUMBER	(31):	
PRIORITY DATE	(32):	
INVENTOR(S)	(72):	Toyonobu Mizutani Akisato Katasaka Kouichi Itoh Touichiro Izawa
APPLICANT(S)	(71):	Ohtake Glass K.K. Synthetic Chemical Laboratories
DESIGNATED CONTRACTING STATES	(81):	
TITLE	(54):	Heat-Resistant Coating
FOREIGN TITLE	[54A]:	Tainetsu Toryou

Specification

1. Title of Invention

Heat-Resistant Coating

2. Scope of Claims

1. A heat-resistant coating comprised of at least a silicone resin and devitrified mica glass.

2. A heat-resistant coating according to Claim 1, which coating contains fluorine gold mica.

3. A heat-resistant coating according to Claim 1 or 2, which coating contains a mineral with a naturally layered structure.

4. A heat-resistant coating according to Claim 1, 2 or 3, which coating contains glass frits.

3. Detailed Description of the Invention

The present invention pertains to heat-resistant coating capable of forming devitrified ceramic film in a high temperature range.

Compositions employing a silicone resin as a vehicle and various inorganic powders added thereto to improve thermal characteristics have heretofore been known as heat-resistance coatings at higher temperatures of no less than 300°C. The types of inorganic powders used include powders of such metals as aluminum and zinc; such naturally

illegible minerals as natural mica, talc, and montmorillonite; and such other ceramic substances as carbon, carbides, nitrides, borides, silicates, metal oxides, and hyaline substances.

While such heretofore used combinations of silicone resins and inorganic powders are somewhat effective in increasing heat resistance, inorganic powder content of 30% or more causes a decline in the faculty of the coating film formed on the object to be coated. In particular, heating the coating to a temperature of 400°C or higher for application reasons results in the sublimation of the organic components of the silicone resin serving as the vehicle evaporate, and while said components transition into an inorganic substance with a siloxane structure (Si-O-Si-O), the siloxane bonds are weak during this period and no bonding whatsoever occurs with the aforementioned inorganic powders; hence, the coating film strength declines, resulting in the formation of minute cracks. Further, such degradation as chalking and peeling occur at temperatures of 500°C and

/2

higher, resulting in the loss of performance as a heat-resistant coating film.

A known method for improving on the degradation

phenomenon involves adding glass frits, having melting points ranging from low to high, and preventing the degradation of coating films through the softening and fusing of glass frits in the temperature range wherein silicone resins transition into siloxanes (300°C ~ 500°C). However, because the bonding *illegible* according to this method is dependent on hyaline matrix, such factors as the wettability with inorganic powders, difference in expansion coefficient with the object to be coated, and creeping due to repeated cooling and heating cause stress, resulting in the degradation of the coating film over time.

The present invention improves on the aforementioned problems presented by conventional heat-resistant coating and is characterized by comprising at least a silicone resin and devitrified mica glass (hereinafter abbreviated as "mica glass").

The present invention seeks to form a devitrified ceramic coating film by ceramifying a silicone resin with devitrified mica glass at a high temperature at which the resin decomposes, thereby providing a heat-resistant coating that is not damaged by repeated heating and cooling over extended period in the *illegible* range, and, the ceramification reaction in this case being a solid phase reaction between siloxane and mica glass, said coating film

is basically different in nature from the simple conventional glass fusion coating film formed from natural mica, siloxane, and glass frits.

Devitrified mica glass is a substance with the composition $K_2O-MgO-MgF_2-SiO_2$ that is obtained by melting a batch with a molar ratio of 0.5 K_2O :1.5 MgO : MgF_2 :4 SiO_2 at a temperature of 1300°C or higher. For example, when a 1400°C melt is cooled to 1000°C in 10 ~ 20 minutes, 70 ~ 80% of devitrified ceramic comprising precipitated potassium tetra silicon mica $[KMg_{2.5}(Si_4)_{10}F_2]$ can be obtained in the glass, though the amount varies depending on the size of the illegible cluster. The ratio of said vitrified ceramic to the glass components increases as the cooling rate increases.

Since mica glass is a ceramic formed by the precipitation of potassium tetra silicon mica crystals, the melt thereof is characterized by the fact it is less inclined to generate mica crystals compared to melts comprising fluorine mica of other compositions, and that over-cooling easily results in the formation of 100% to about 5% glass.

In the present invention, the sintering of mica glass and siloxane is caused to start at about 900°C the joint action of the half melted and strongly alkaline mica to

melt and vitrify non-crystalline SiO_2 and of the small amount of gas comprising such substances as evaporated fluorides, KF , and SiF_4 , to lower the melting point of SiO_2 . Further, because the expansion coefficient of mica glass is $4 \sim 5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ as opposed to the $10 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ or higher of numerous other fluorine, natural and other types of mica, coating films containing mica glass are not stressed much by rapid heating and cooling and, therefore, are not damaged.

In the present invention, it is desirable to add a fluorine gold mica or gold mica, white mica, or such naturally layered minerals as vermiculite to the formulation comprising silicone resin and mica glass in order to stably conduct the ceramification reaction of siloxane and mica glass and to improve the flexibility of the coating film in the low temperature range as well as the thermal characteristics thereof in the high temperature range.

This is to say that the aforementioned mica glass, which can be sintered with siloxane from about 600°C , has relatively little cleavability although it excels in sinterability. Hence, the coating film is formed so that the structure thereof is such that the flakes with larger aspect ratios are overlap with each other and are parallel

with the surface of the object to be coated.

Fluorine gold mica being a typical fluorine mica that has high crystallinity and high cleavability, those of a satisfactory aspect ratio of about 50 ~ 100 are easily obtainable by pulverization. Through a solid reaction, mica glass begins to form a solid solution and ceramifies from about 1100°C. Since this ceramification takes place when the mica glass is in a half-melted state, the coating film does not flow and is stable. Flakes with satisfactory aspect ratios are also easily obtainable from natural and other mica, and they impart flexibility to the coating film as well as *illegible* with the other components within the coating film composition due to the glass *illegible* solution produced between mica glass and siloxane at high temperatures. Any naturally layered mineral that can be

/3

cleaved satisfactorily may be used, examples of which include gold mica, white mica, vermiculite and other types of minerals, and the effect thereof does not change regardless of whether they are used alone or in combination with fluorine fold mica.

In the present invention, it is desirable to add glass frits to the composition comprising silicon and mica glass. This is to say that the addition of glass frits prevents

the peeling of and the occurrence of cracks in the coating film at temperatures from 350°C, when the silicone resin begins to form siloxane, to about 900°C, when siloxane begins to turn into a solid solution, as well as take part in the ceramification reaction of the fluorine mica and the siloxane series at a temperatures of 900°C and higher, thereby forming a devitrified ceramic coating film.

Examples of the types of glass frits used include borates, borosilicates, *illegible*, and sulfosilicates. The softening points of these glass frits range from 350°C to about 900°C and may be selected as necessary, depending on such factors as the temperature range at which the coating film is to be used and the material comprising the object to be coated. Mica glass mutually fuses with borates and phosphates from when it is in a half-melted state. It is from this fused glass that potassium tetra silicon precipitates out during cooling. This is similar to the formation process of the so-called devitrified. Of course, the newly formed fused glass fusion bonds closely also with fluorine gold, natural, and other mica. Because a ceramic coating film thus formed has a composition wherein the homogeneous overlap of flakes with high flexibility and satisfactory aspect ratios are closely and strongly bonded with the object to be coated with the devitrified glass

serving as the bonding matrix, it is heat resistant and has excellent heat-cool cycle endurance.

As regards the type of silicone resin used in the present invention, any of straight silicon, modified silicon, and cold blended types may be used. However, the content of the siloxane that ultimately participates in the ceramification reaction is desirably no less than 1/20 of inorganic substances other than the resin, and other *illegible* are selected depending on the conditions of use for the coating. This is to say that silicon rubbers are used for application on inorganic *illegible* cloth that maintains flexibility at ambient temperatures and is exposed to extreme temperature changes (e.g., coming into contact with sparks of fire, droplets of molten metal, and arc), cold blends with other *illegible* resins are used in fireproofing coating for large objects that cannot be subjected to thermal curing treatment (e.g. ships, internal combustion *illegible*, and *illegible*), and silicone resins with a high siloxane content are used in such applications where the use temperature is 500°C or higher and those that have undergone the ceramification reaction according to the present invention are used from the beginning.

The formulation composition of the present invention is based on combinations of 5 ~ 90% silicon resin (solid base)

and 95 ~ 10% mica glass, to which fluorine gold mica, naturally layered minerals, glass frits, and other substances are added. Color pigments, extender pigments, and metal powders may be added to the composition as needed to the extent they do not undermine the coating film characteristics.

As explained above, the heat resistant coating according to the present invention is not limited to use in temperatures ranging from ambient temperatures to temperatures at which silicone resins decompose, it can also be used in high temperature ranges of up to about 1000°C. In this case, the basic reaction involves the formation of a solid solution of siloxane and mica glass comprising the composition; a ceramic coating film having devitrified glass matrix containing glass frits is formed on the object to be coated; and said coating film has a composition wherein flexible flakes overlap and is equipped with flexibility, heat resistance, shock resistance, and endurance against heating-cooling cycles repeated over prolonged period.

Working examples of heat-resistant coating according to the present invention are shown hereinbelow.

Example 1

Mica Glass: A 0.5 K₂O:1.5 MgO:LlMgF₂:4 SiO₂ formulation was

melted at 1,450°C ~ 1,500°C, the melt was cooled in air to 1,000°C in 20 minutes, a synthetic clump containing approximately 80% of $\text{KMg}_{2.5}(\text{Si}_4)_{10}\text{F}_2$ crystals and 20% of glass was obtained, and said clump was pulverized for use as raw material.

A coating was prepared with, on the basis of weight, 300 parts of xylene as the solvent and 100 parts of a composition comprising 30% silicone resin (solid basis; KR275 of Shin Etsu Chemical Co., Ltd.), 58% mica glass that passed through a 325 mesh, 6% zinc oxide, 4% black pigment ceramic, 1.5% non-ion dispersing agent, and 0.5% zinc octylate.

/4

Said coating was applied on one surface of an iron sheet 100 mm x 100 mm x 1.5 mm in size, blow dried for approximately 60 minutes, and subsequently cured by heating at 180°C for 30 minutes to obtain a coating film 0.15 mm in thickness. It was heated from 200°C to 500°C in 60 minutes, from 500°C to 900°C in 30 minutes, and at 900°C for 30 minutes. The coating film obtained was a ceramic film having a smooth surface and grayish black in color. A heating-cooling test was performed, wherein placement in a 400°C electric furnace for 10 minutes, removal therefrom into air, and cooling as is for 10 minutes constituted one

cycle. Although the test was repeated for 20 cycles, no damage was observed on the coating film.

Example 2

Mica Glass: The same one as in Example was used.

Fluorine Gold Mica: Fluorine gold mica was wet milled in a ball mill for 48 hours, water *illegible*, and said mica that passed through a 200 mesh was collected. The average particle diameter of the mica was 58 μ , and the aspect ratio in the 50 ~ 100 range according to the observation of an electron micrograph.

Natural Mica: Tinolite (a phlogopite) from Quebec, Canada that passed through a 200 mesh. The average particle diameter was 47 μ , and the aspect ratio in the 60 ~ 120 range according to the observation of an electron micrograph.

(A) A coating was prepared with, on the basis of weight, 250 parts of 1,1,1-trichlorethylene as the solvent and 100 parts of a composition comprising 30% silicone resin (solid basis; KR-2038 of Shin Etsu Chemical Co., Ltd.), 36% mica glass that passed through a 325 mesh, 20% fluorine gold mica that passed through a 200 mesh, 7% zinc oxide, 5% phthalocyanine blue pigment, 1% dispersing agent, and 1% coating film modifier.

(B) Of the composition in (A) above, the fluorine gold mica

was replaced with 20% natural mica that passed through a 200 mesh. The rest of the composition is the same as in (A).

Coating A and B were each applied on one surface of an electrical insulating glass cloth (JIS R3414) ECG 30 A (plain woven, 0.3 mm in thickness) in an amount of 400 g/m², blow dried for 30 minutes, subsequently cured by heating at 180°C for 30 minutes to form a coating film 0.27 mm in thickness, and the film was used as a sample bundling tape for fire-resistant electrical wires. Coated tapes A and B did not develop a fold, even when bent at a 180° angle. 10 heat-resistant electrical wires (22 ml of cross-linked polyethylene electrical wires) were bundled together and wrapped three times with the tape and heated with a Bunsen burner so that the surface temperature of the tape reached about 900 ~ 1,000°C. Coating films A and B were both nonflammable, a ceramic film had developed on the heated area.

Example 3

The same mica glass and fluorine gold mica as in Example 2 were used.

(A) A coating was prepared with, on the basis of weight, 250 parts of 1,1,1-trichlorethylene as the solvent and 100 parts of a composition comprising 30% silicone resin (solid

basis; KR-275 of Shin Etsu Chemical Co., Ltd.), 25% mica glass that passed through a 325 mesh, 25% fluorine gold mica that passed through a 200 mesh, 15% phosphate frit (softening temperature of 650°C) that passed through a 200 mesh, 1% dispersing agent, and 1% coating film modifier.

Said coating was applied on one surface of an iron sheet 100 mm x 100 mm x 1.5 mm in size, blow dried for approximately 30 minutes, and subsequently cured by heating at 180°C for 30 minutes to form a coating film 0.15 mm in thickness. The iron sheet was heated in an electrical furnace from 200°C to 500°C in 60 minutes, from 500°C to 900°C in 30 minutes, and at 900°C for 30 minutes. The coating film on the iron sheet was an enamel-like ceramic film that was milky white in color. A heating-cooling test was performed, wherein placement in a 500°C electric furnace for 10 minutes, removal therefrom into air, and cooling as is for 10 minutes constituted one cycle. Although the test was repeated for 20 cycles, no damage was observed on the coating film.

(b) A coating was prepared with, on the basis of weight, 250 parts of combined xylene-MIBK solvent (7:3) as the solvent and 100 parts of a composition comprising 40% epoxy-altered silicone resin (solid basis; 81001 of Shin Etsu Chemical Co., Ltd.), 20% mica glass that passed

through a 325 mesh, 15% natural mica that passed through a 200 mesh, 8 % ceramic black that passed through a 325 mesh, 1% dispersing agent, and 1% coating film modifier. Said coating was applied on one surface of a copper sheet 200 mm x 200 mm x 2 mm in size, blow dried for approximately 2 hours, and subsequently cured by heating at 150°C for 30 minutes. The coated surface was heated with a gas burner for 30 minutes so that the surface temperature will reach from 550°C ~ 600°C, and thereby formed a black ceramic coating film. Although it was heated in a gas furnace so

/5

that the surface of the ceramic coating film will be 300°C ~ 350°C at all times for 300 hours, the coating film did not show any signs of damage, such as cracks and peeling.